

Electron impact investigation of electronic excitations in furan, thiophene, and pyrrole

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The electronically excited states of furan, thiophene, and pyrrole have been studied by electron impact at scattering angles from 0° to 80°, and impact energies of 30 and 50 eV. Low-lying features at 3.99 and 5.22 eV in furan, 3.75 and 4.62 eV in thiophene, and 4.21 eV in pyrrole are identified as singlet → triplet transitions. The locations and, for furan and thiophene, the energy splittings of these excitations suggest that they are analogous to the lowest $\pi \rightarrow \pi^*$ singlet → triplet transitions in benzene, and that these heterocycles have appreciable aromatic character. A weak feature observed in pyrrole at 5.22 eV is attributed to an optically forbidden singlet → singlet transition. In all three molecules, transitions to several superexcited states are observed.

I. INTRODUCTION

The lowest singlet → triplet transitions in the five-membered heterocycles furan (C₄H₄O), thiophene (C₄H₄S), and pyrrole (C₄H₄NH) have been detected in an electron impact investigation of their excited electronic states. These molecules are of considerable importance in synthetic organic chemistry,^{1,2} in the preparation of various drugs and polymers, and in biochemistry as components of many biologically active molecules, such as chlorophyll, vitamin B₁₂, bile pigments, and biotin. They have been the subject of a great many electronic structure and energy calculations.³⁻¹⁴ They have served as useful systems for the investigation of such questions as the validity of the σ , π separation approximation, the amount of d orbital participation in bonding, and the degree of aromaticity. Their ultraviolet absorption spectra¹⁵⁻³⁶ have been investigated for more than sixty years, but information on singlet → triplet absorptions is scattered and conflicting. In 1958, Heckman²⁹ reported that none of these three heterocycles exhibited emission of light either by phosphorescence or fluorescence, and indicated the need for further studies of these molecules.

The method of low-energy, variable angle electron impact spectroscopy³⁷⁻⁴⁰ has been used successfully to investigate spin-forbidden and other electric dipole-forbidden transitions in molecules. Recently, several series of chemically similar compounds have been studied by this technique,³⁹ and the information obtained by such "chemical scanning" investigations appears to be of great utility in the interpretation of electronic spectra. An important feature of the electron impact technique is the sensitivity^{37,38,40b} of the shape of the differential cross section (DCS) versus scattering angle curve for inelastic scattering to the change in spin quantum number of the target molecule. Spin-allowed processes have a sharply forward-peaked DCS, while spin-forbidden processes have a more nearly isotropic DCS, for impact energies, E_0 , between 20 and 50 eV above excitation threshold. For this reason, the ratio of the intensity of a spin-forbidden excitation to that of a spin-allowed one is found to increase by about two orders of magnitude as the scattering angle Θ increases from 0° to 80°. ³⁷⁻⁴⁰ Moreover, this ratio is usually found to be

larger at low impact energies than at high ones.^{39,40} In contrast, the ratio of intensities of two electric dipole-allowed transitions is nearly independent of angle, usually varying by less than a factor of 3 over the angular range 0°–80°. ³⁸⁻⁴⁰

II. EXPERIMENTAL

The apparatus employed in this study has been described previously.^{37,38,40} Briefly, an electron gun injects a beam of electrons into a hemispherical electrostatic energy monochromator with a mean radius of 3.81 cm. The energy-selected beam scatters off the target gas or vapor contained in a flexible bellows scattering chamber, and the scattered electrons are energy-analyzed by an analyzer identical to the monochromator. A continuous dynode electron multiplier serves as detector, and the output pulses are amplified, shaped, and stored in a 1024-channel scaler. The impact energy E_0 is given nominally by the applied voltage difference between the filament center and the scattering chamber. E_0 differs from the true impact energy mainly due to contact potentials (1–2 eV).^{37b,41} The energy loss ΔE of any feature is determined by the difference between the voltage applied to the deceleration element which follows the scattering chamber when the feature is detected and that applied to the same element when the elastic peak is detected. This sweep voltage difference is measured with a digital voltmeter. Comparison with optical excitation potentials indicates that the energy-loss scale as determined in this manner is accurate to 0.01 eV, in spite of the uncertainty in E_0 . Since in our work E_0 is well above resonant energies, the angular distributions are insensitive to its exact value. The spectrum is repeatedly scanned for a total accumulation time of 4–6 h, or until the signal/background noise ratio is at least 5:1 on the weakest feature of a spectrum. However, some molecules, such as pyrrole, appear to contaminate the electron optical surfaces more than others, leading to high backgrounds, and in such cases a signal/background ratio of 2:1 is considered acceptable.

In the present experiments, the electron energy-loss spectra of furan, thiophene, and pyrrole were investigated from 0 to 15 eV energy loss, at E_0 values of 30

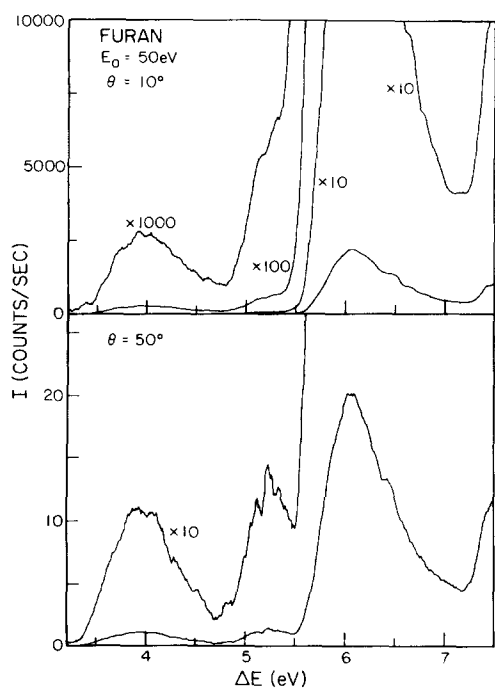


FIG. 1. Electron energy-loss spectrum of furan at $\Theta = 50^\circ$ and $\Theta = 10^\circ$; 50 eV incident electron energy; 0.11 eV FWHM (full width at half-maximum of elastic peak).

and 50 eV, and $\Theta = 0^\circ$ to 80° . Incident electron beam intensities into the scattering chamber were typically 5×10^{-8} A, and sample pressures ranged from 4 mtorr to 7 mtorr, as indicated by an uncalibrated Schulz-Phelps ionization gauge. Energy resolution, as measured by the full width at half-maximum (FWHM) of the elastic peak, was chosen in this study in the range from 0.10 to 0.15 eV, with a few spectra run at higher resolution, 0.06 to 0.08 eV.

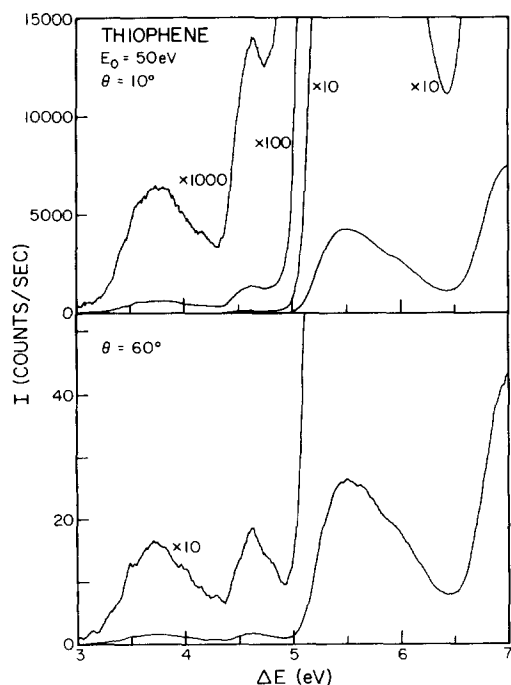


FIG. 2. Electron energy-loss spectrum of thiophene at $\Theta = 60^\circ$ and $\Theta = 10^\circ$; 50 eV incident electron energy; 0.15 eV FWHM.

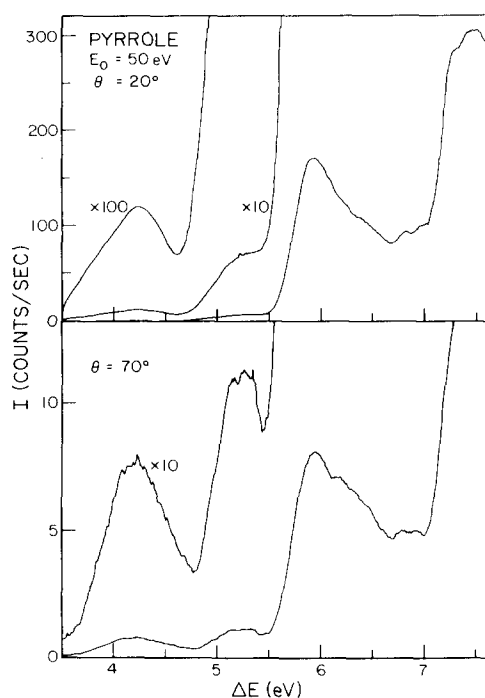


FIG. 3. Electron energy-loss spectrum of pyrrole at $\Theta = 70^\circ$ and $\Theta = 20^\circ$; 50 eV incident electron energy; 1.4×10^{-7} A incident beam current; 6.4 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; 0.15 eV FWHM.

The furan, obtained from Matheson, Coleman, and Bell, was of unspecified purity, but had a specified boiling point range of 31 to 32°C . Gas chromatographic analysis indicated that the sample purity was better than 99%. The thiophene sample was obtained from the Aldrich Chemical Co., and had a specified purity of 99+%. Samples of pyrrole from two different sources were used. Most of the spectra were taken using Eastman Kodak Co. practical grade pyrrole. It was analyzed with a gas chromatograph-mass spectrometer system. Using a Porapak-Q column at a temperature of 140°C , we identified the principal impurity as pyrrolidine, at a level of less than 5%. Pyrrolidine has a relatively small extinction coefficient²⁷ ($\epsilon < 400$ l mole⁻¹ cm⁻¹) in the excitation energy range below 5.5 eV, of primary interest in the present work. In addition, spectra were run with pyrrole obtained from the Aldrich Chemical Co. with a specified purity of 98%. No appreciable qualitative or quantitative differences in the spectra obtained with samples from these two sources were observed. All samples were subjected to several liquid nitrogen freeze-pump-thaw cycles prior to use.

III. RESULTS AND DISCUSSION

A. Low energy-loss region

Figures 1-3 display the low energy-loss part of the spectra of all three molecules at an impact energy of 50 eV and at both low and high scattering angles. The location of the absorption maxima and the operational Franck-Condon range (outside of which we can no longer detect the transition) of each band system are given in Table I. The location of the maxima are believed ac-

TABLE I. Triplet state energies of furan, thiophene, and pyrrole.

Molecule	Position of absorption maximum (eV)	Operational Franck-Condon Range (eV)	Optical observations (eV) ^a	Theoretical calculations (eV)
Furan	3.99	3.3-4.9	4.1-5.1 ^b	4.17 ^k
			4.3-5.2 ^c	4.33 ^l
	5.22	4.7-5.7	3.9-4.5 ^d	4.76 ^k
			4.0-5.2 ^e	5.05 ^l
Thiophene	3.75	3.15-4.5	3.90, 3.96 ^g	2.3 ^m
				3.42 ^k
	4.62	4.3-5.1	3.7-4.6 ^b	3.6 ^m
			4.6 ^h	4.18 ^k
Pyrrole	4.21	3.6-5.0	4.26 ^j	3.29 ⁿ
			3.1-4.7 ^b	3.75 ^o
			4.2-4.8 ^c	4.0 ^p
				4.08 ^q
				4.10 ^k
				4.98 ^r

^aThe numbers in this column refer to observed absorptions, only a few of which were assigned to singlet-triplet transitions and some of which may be due to impurities.

^bReference 34.

^cReference 16.

^dReference 33.

^eReference 20.

^fReference 30.

^gReference 26.

^hReference 19.

ⁱReference 18.

^jReference 17.

^kReference 6.

^lReference 12.

^mReference 13.

ⁿReference 5.

^oReference 9.

^pReference 8.

^qReference 4.

^rReference 7.

curate to ± 0.03 eV, while the Franck-Condon limits are reproducible to ± 0.1 eV. These band onsets do not necessarily correspond to the 0-0 transitions.

In furan, the lowest observed inelastic feature occurs in the region from about 3.3 to 4.9 eV (Fig. 1). The measured value of the maximum intensity of this transition varied over the range 3.89 to 4.02 eV, depending on the resolution and the signal/noise ratio of the particular spectrum. Many spectra indicate the presence of two, and sometimes three, poorly resolved vibronic bands at about 3.89, 3.99, and 4.09 eV energy loss. Our best estimate for the position of the maximum of the central band is 3.99 eV. In Fig. 1, the first two bands are not resolved and result in a single peak having a maximum at 3.94 eV in addition to the one at 4.09 eV. The second transition in furan has a maximum intensity at 5.22 eV. Figure 4 displays the ratio of the intensities of each of these transitions to that of the optically allowed transition at 6.06 eV energy loss. These intensity ratios are obtained from the relative areas under the deconvoluted absorption features.⁴⁰ At $E_0 = 50$ eV, the ratio of the intensity of the first transition to that of the 6.06 eV feature increases by a factor of about 45 as θ increases from 10° to 80° . The corresponding ratio for the second feature also increases by a factor of 45. A less pronounced increase with scattering angle was observed for both ratios at $E_0 = 30$ eV. For all angles studied, the ratio at $E_0 = 30$ eV was larger than at $E_0 = 50$ eV. This energy and angle dependence is charac-

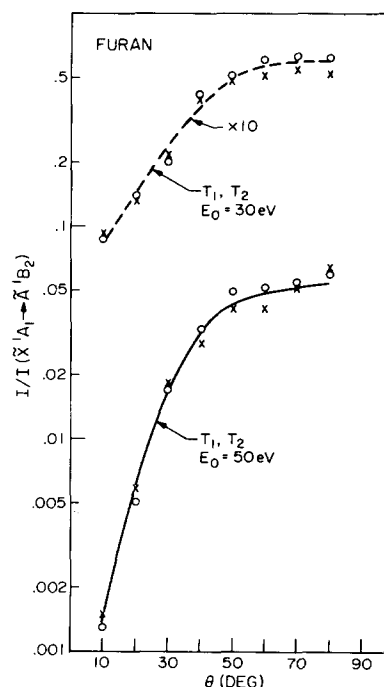


FIG. 4. Ratio of the intensities (I) of the two lowest observed electronic transitions in furan to that of the optically allowed transition $\bar{X}^1A_1 \rightarrow \bar{A}^1B_2$ as a function of scattering angle θ at incident electron energies of 30 eV (dashed line) and 50 eV (solid line). The excited states for the curves shown are the 3.99 eV triplet T_1 (O), and the 5.22 eV triplet T_2 (X). The 30 eV curves have been scaled by a factor of 10.

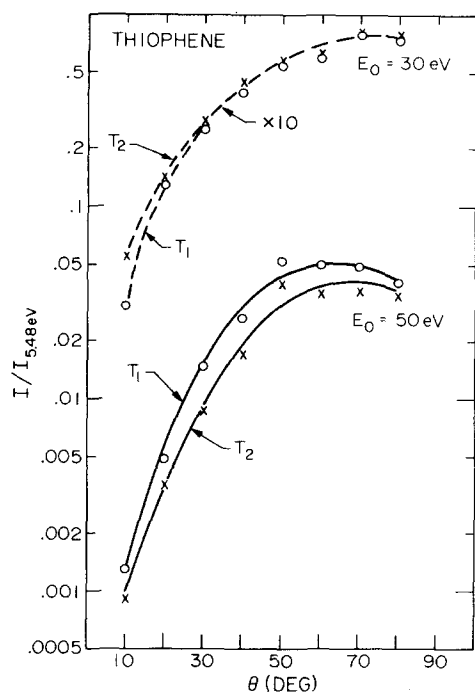


FIG. 5. Ratio of the intensities (I) of the two lowest electronic transitions in thiophene to that of the optically allowed transition at 5.48 eV ($I_{5.48}$) as a function of θ at incident electron energies of 30 eV (dashed line) and 50 eV (solid line). The excited states for the curves shown are the 3.75 eV triplet T_1 (O), and the 4.62 eV triplet T_2 (X). The 30 eV curves have been scaled by a factor of 10.

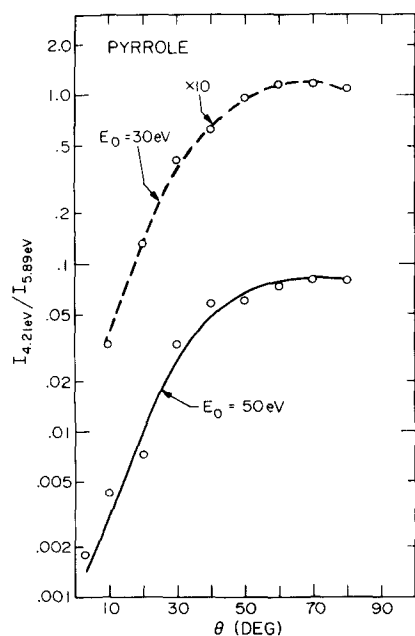


FIG. 6. Ratio of the intensity of the 4.21 eV singlet \rightarrow triplet transition ($I_{4.21}$) in pyrrole to that of the optically allowed transition at 5.89 eV ($I_{5.89}$) as a function of θ at incident electron energies of 30 eV (dashed line) and 50 eV (solid line). The 30 eV curve has been scaled by a factor of 10.

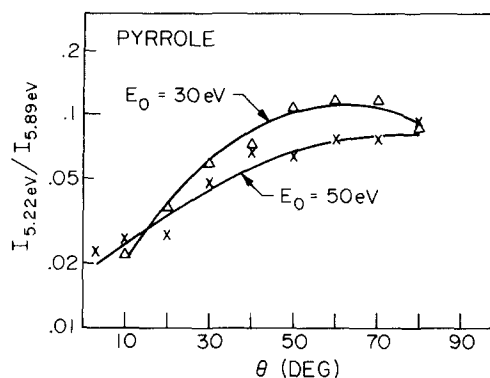


FIG. 7. Ratio of the intensity of the 5.22 eV transition ($I_{5.22}$) in pyrrole to that of the optically allowed transition at 5.89 eV ($I_{5.89}$) as a function of θ at incident electron energies of 30 eV (Δ) and 50 eV (X).

teristic of spin-forbidden transitions,³⁷⁻⁴⁰ and we assign the two lowest-lying features to singlet-triplet excitations in furan.

The low energy-loss region of the thiophene spectrum shown in Fig. 2 resembles that of furan, but is somewhat red-shifted and has a smaller energy splitting between the two lowest features. The lowest observed inelastic feature in thiophene occurs in the region from 3.15 to 4.5 eV energy loss. As in furan, the energy loss corresponding to the maximum intensity of this transition varied, ranging from 3.62 to 3.82 eV. In most spectra, only one peak is observed at about 3.75 eV. However, a few spectra appear better resolved, and indicate the presence of two vibronic peaks of approximately equal intensity at about 3.66 and 3.82 eV. Therefore, the 3.75 eV value probably represents an average of these two energies. The second transition in thiophene has a maximum intensity at 4.62 eV. The angular and impact energy dependence (Fig. 5) of the intensity ratios of both transitions with respect to the singlet-singlet absorption at 5.48 eV are similar to those of the corresponding transitions in furan. We therefore assign both low-lying features in thiophene to singlet-triplet excitations.

Figure 3 displays the low energy-loss region in pyrrole. The energy-loss values of the first three observed transitions are similar to those of furan. The first feature in pyrrole has a maximum intensity at 4.21 eV, while that of the second transition occurs at 5.22 eV. However, the angular dependence of the ratios of the intensities of each of these two transitions to that of the optically allowed transition at 5.89 eV is noticeably different (Figs. 6, 7). At $E_0 = 50$ eV, the intensity ratio associated to the 4.21 eV transition increases by a factor of 45 over the angular range 3° to 80° (Fig. 6). The intensity ratio for the 5.22 eV transition increases by only a factor of 4 over the same angular range (Fig. 7). Similarly, at $E_0 = 30$ eV, the intensity ratio for the lowest transition increases by a factor of about 20 as θ varies from 10° to 80° , whereas that for the second transition increases by a factor of 5. The behavior of these ratios indicates that the first excitation is indeed due to a singlet-triplet excitation. However, the sec-

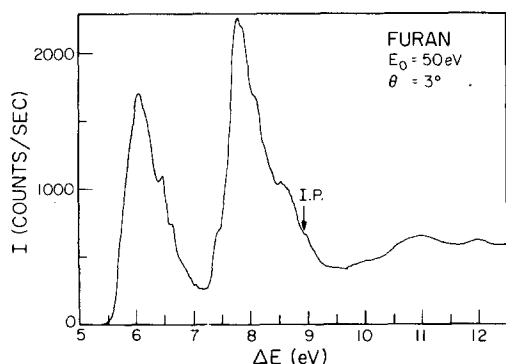


FIG. 8. Electron energy-loss spectrum of furan in the 5.0 to 12.5 eV energy-loss region at $\Theta = 3^\circ$; 50 eV incident electron energy; 0.11 eV FWHM. The position of the lowest ionization potential (I.P.) is indicated.

ond feature probably corresponds to a weak, dipole-forbidden, singlet-singlet excitation.⁴⁰ Previous studies³⁸⁻⁴⁰ have indicated that if the ratio of the intensity of an unknown transition to that of an electric dipole-allowed transition increases with angle by a factor of 4 to 7 for several different impact energies, then the unknown transition is probably a dipole-forbidden, spin-allowed excitation. This interpretation is consistent with the fact that the 5.22 eV feature in pyrrole was observed optically³⁵ in a highly purified sample with an extinction coefficient ϵ of 30 l mole⁻¹ cm⁻¹, which is one to two orders of magnitude higher than the largest singlet-triplet optical extinction coefficients⁴² in molecules consisting of low atomic weight atoms, but several orders of magnitude smaller than coefficients⁴² associated with dipole-allowed optical excitation. Finally, to preclude the possibility that the second inelastic feature we observe in pyrrole may be due to the pyrrolidine impurity present in the sample, we compared our spectra with recently obtained electron impact spectra⁴³ of pyrrolidine. These pyrrolidine spectra corroborate the optical spectra,²⁷ and indicate that the 5.22 eV feature in question is indeed due to pyrrole.

Table I also contains a summary of previously reported optical observations of low-lying transitions in furan, thiophene, and pyrrole. Mason³⁰ reported a weak ($\epsilon = 0.02$ l mole⁻¹ cm⁻¹) absorption in furan at 4.96

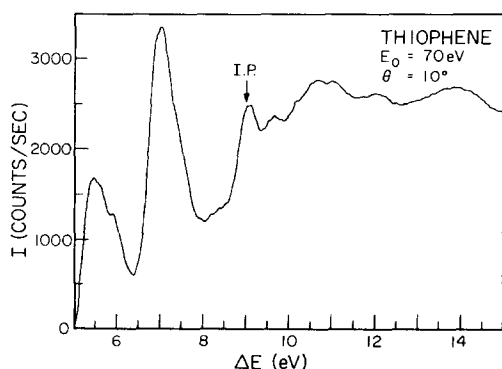


FIG. 9. Electron energy-loss spectrum of thiophene in the 5.0 to 15.0 eV energy-loss region at $\Theta = 10^\circ$; 70 eV incident electron energy; 5×10^{-8} A incident beam current; 0.11 eV FWHM. The position of the lowest ionization potential (I.P.) is indicated.

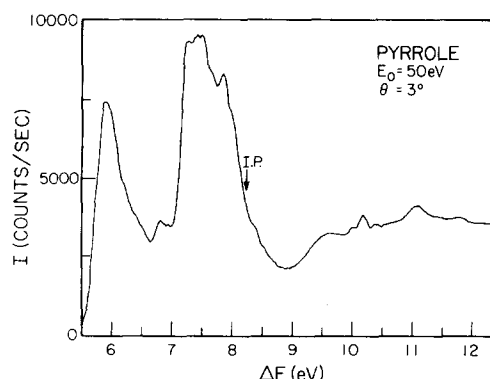


FIG. 10. Electron energy-loss spectrum of pyrrole in the 5.5 to 12.5 eV energy-loss region at $\Theta = 3^\circ$; 50 eV incident electron energy; 1.2×10^{-7} A incident beam current; 5.6 mtorr sample pressure from an uncalibrated Schulz-Phelps ionization gauge; 0.15 eV FWHM. The position of the lowest ionization potential (I.P.) is indicated.

eV, which was attributed to either a forbidden transition or an impurity. There have also been other reports^{16,20,33,34} in the literature of a long wavelength tail in the 4-5 eV region of furan. In thiophene, Padhye and Desai²⁶ reported two weak ($\epsilon = 0.048$ l mole⁻¹ cm⁻¹) maxima at 3.90 and 3.96 eV, which they tentatively assigned as one or possibly two singlet-triplet transitions. Several other authors^{16,18,19,34} have reported a weak feature in thiophene at about 4.6 eV. For pyrrole, Boryniec and Marchlewski¹⁷ reported a weak band at 4.26 eV. Mullen and Orloff³⁵ have examined *uv* absorption in highly purified pyrrole, and conclude that the absorption at about 5.2 eV is due to an optically forbidden singlet-singlet transition in pyrrole, not an impurity. Horváth and Kiss^{31,34} analyzed previously reported spectra of all three molecules and concluded that the long wavelength bands observed between 4 and 5.3 eV were primarily due to benzene and toluene impurities. After purifying their samples repeatedly, they concluded³⁴ that the weak ($\epsilon = 0.1$ l mole⁻¹ cm⁻¹) shoulders which remained in the 4-5 eV region were due to singlet-triplet transitions.

Comparing previous literature observations with the present results, we find that, to our knowledge, the two

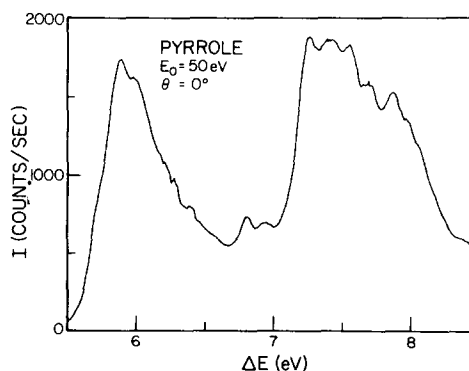


FIG. 11. High resolution electron energy-loss spectrum of pyrrole in the 5.5 to 8.5 eV energy-loss region at $\Theta = 0^\circ$; 50 eV incident electron energy; 1.5×10^{-8} A incident beam current; 5.4 mtorr sample pressure reading from an uncalibrated Schulz-Phelps ionization gauge; 0.07 eV FWHM.

TABLE II. Higher excited electronic states of furan, thiophene, and pyrrole.

Molecule	Excited state ^a	Optical observations (eV) ^b	Present results (eV) ^{b,c}
Furan	\bar{A}^1B_2	6.06 ^d	6.06 ± 0.02
	\bar{B}^1A_1	6.47 ^d , 6.61 ^d	6.44 ± 0.03, 6.61 ± 0.03
	\bar{C}^1A_1	7.39 ^{d,e}	7.42 ± 0.03
	1A_1 or 1B_2	7.79 ^d	7.82 ± 0.04
	Rydberg ^g	8.01 ^e	8.05 ± 0.03
	Rydberg ^g	8.50 ^e	8.52 ± 0.03
	Superexcited	...	11.0 ± 0.1
	Superexcited	...	11.95 ± 0.05
	\bar{A}^1A_1 or 1B_2	5.30 ^f , 5.41 ^g , 5.53 ^g	5.48 ± 0.05
	\bar{B}^1A_1 or 1B_2	5.99 ^{f,h}	5.93 ± 0.03
Thiophene	\bar{C}^1A_1 or 1B_2	6.90 ^h , 6.98 ^h , 7.05 ^h	7.05 ± 0.03
	5R ^h	8.22 ^h	8.21 ± 0.02
	5R + 8 ^h	8.39 ^h	8.39 ± 0.02
	Superexcited	...	9.08 ± 0.03
	Superexcited	...	9.65 ± 0.05
	Superexcited	...	10.20 ± 0.05
	Superexcited	...	10.7 ± 0.1
	Superexcited	...	11.1 ± 0.1
	Superexcited	...	12.1 ± 0.1
	Superexcited	...	13.9 ± 0.1
Pyrrole	1A_1	5.22 ⁱ	5.22 ± 0.03
	\bar{A}^1B_2	5.88 ⁱ , 5.96 ⁱ	5.89 ± 0.04, 5.98 ± 0.03
	Rydberg ^k	6.23, 6.32 ⁱ	6.2–6.5
	\bar{B}^1A_1	6.78 ⁱ	6.80 ± 0.03, 6.93 ± 0.03
	\bar{C}^1B_2 or 1A_1	7.21 ⁱ	(7.26 ± 0.03, 7.43 ± 0.03, ^m 7.54 ± 0.03, 7.69 ± 0.03, ^m 7.86 ± 0.03)
	Superexcited	...	9.63 ± 0.1
	Superexcited	...	10.18 ± 0.05
	Superexcited	...	11.06 ± 0.05
	Superexcited	...	11.76 ± 0.05
	Superexcited	...	11.76 ± 0.05

^aMost excited state symmetries are uncertain. See Ref. 4–14.

^bVertical transition energies.

^cUncertainties represent the range of values observed.

^dReference 20.

^eReference 28.

^fReference 24.

^gReference 21.

^hReference 36.

ⁱReference 35.

^jReference 32.

^kReference 48.

^lReference 27.

^mThese five bands may belong to the same electronic transition.

excitations we observe in furan have not been observed before. However, the absorptions reported by Padhye and Desai²⁶ in thiophene, and by Boryniec and Marchlewski¹⁷ in pyrrole may correspond to the singlet–triplet transitions which have been measured and assigned in the present study. The feature repeatedly reported^{16, 18, 19, 34} at about 4.6 eV in thiophene may be the second singlet–triplet transition. However, it is also possible that these optical absorptions are due to benzene and toluene impurities, as suggested by Horváth and Kiss.^{31, 34} Fortunately, the electron impact technique is not plagued with impurity problems insofar as identification of singlet–triplet transitions is concerned, since these features can readily be distinguished by their angular and impact energy dependence from singlet–singlet transitions in impurities. Singlet–triplet transition intensities associated to impurities at a level of a few percent or less would be at least one order of magnitude lower than the intensities of the transitions we have reported here. In agreement with Mullen and Orloff³⁵, and for the reasons pointed out above, we believe that the transition which we observe in pyrrole at 5.22 eV is most likely due to a weak, singlet–singlet excitation in pyrrole, rather than a strong transition in an impurity molecule.

There have been many theoretical calculations^{3–13} of

the excited manifold of electronic states in furan, thiophene, and pyrrole, some of which^{4–9, 12, 13} have included calculation of triplet state energies. Table I contains the results of some of these studies. The calculations indicate that the lowest two triplet states are probably 3B_1 and 3A_1 , but they are not accurate enough to assign their relative order with any certainty.

The locations of the singlet–triplet transitions reported in this study support a quasiaromatic^{1, 3, 24, 44} model of the electronic structure of these molecules. The first singlet–triplet transition energies in furan, thiophene, and pyrrole do not differ appreciably from that in benzene, 3.95 eV.⁴⁵ The splitting between the first two triplet states in thiophene, 0.9 eV, is about the same as that in benzene, while the splitting between these transitions in furan is somewhat larger, 1.2 eV. An alternative model^{11, 21} of these heterocycles assumes that their electronic spectrum should be analogous to that of conjugated dienes, e.g., *s-cis*-1, 3-butadiene. However, accurate calculations⁴⁶ on *s-cis*-1, 3-butadiene indicate that the lowest triplet state should occur at about 2.95 eV, a value which agrees well with the measured energy, 2.94 eV, of the lowest triplet state in a related molecule, 1, 3-cyclohexadiene.³⁹ The same calculations⁴⁶ on *s-cis*-1, 3-butadiene predict an energy splitting between the first two triplet states of about 2 eV. Calculations⁴⁶ of equivalent accuracy for this splitting in *s-trans*-1, 3-butadiene also agree well with experiment.^{40a} Clearly, our results do not lend support to the diene model of the three heterocycles of interest in this study, insofar as the locations of the lowest triplet electronic states are concerned.

Another result of interest is the apparent absence of any weak, low-lying singlet–singlet transitions in furan or thiophene which could be assigned to an $n \rightarrow \pi^*$ excitation, involving excitation from a nonbonding orbital localized on the heteroatom. This agrees with previous work.³⁰ According to the quasiaromatic model of pyrrole, the aromatic character of the heterocyclic ring would be due to the contribution of the N atom lone pair, and thus pyrrole would have no nonbonding electrons. Therefore, within the framework of this model, the 5.22 eV transition in pyrrole would not due to an $n \rightarrow \pi^*$ transition, but to a $\pi \rightarrow \pi^*$ transition instead.

B. High energy-loss region

Figures 8–11 display the high energy-loss regions of the spectra of furan, thiophene, and pyrrole. Figure 11 is a spectrum of pyrrole taken at higher resolution than Fig. 10, and thus reveals vibronic structure not apparent in the lower resolution spectrum. Our observed peak locations agree well with optical values (Table II). In particular, we observe a transition in thiophene at 5.93 eV (Fig. 9), in agreement with both Milazzo²⁴ and Di Leonardo *et al.*³⁶ This transition was not observed in an earlier study²¹ of the ultraviolet absorption spectrum of thiophene. In each molecule we have also observed transitions to several superexcited states, which lie above the first ionization potential.⁴⁷ These transitions have not been reported previously.

IV. CONCLUSIONS

In summary, an investigation of furan, thiophene, and pyrrole with the technique of low energy, variable angle electron impact spectroscopy has yielded new information about the excited electronic states of these molecules. In this paper, we have provided the first positive identification of low-lying singlet-triplet transitions in furan, thiophene, and pyrrole. Their locations lend support to a heteroaromatic model of these systems, in which a pair of electrons from the heteroatom is delocalized into the π -electron ring. We have found no evidence for any low-lying $n \rightarrow \pi^*$ transitions, but our results do indicate that the lowest singlet-singlet transition in pyrrole is not the transition at 5.89 eV, as is commonly assumed, but is rather a weak, dipole-forbidden transition at 5.22 eV. Finally, we have observed several transitions to previously unreported superexcited states in each of these molecules.

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